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Effect of Natural Rubber Contents on Biodegradation and Water Absorption of Interpenetrating Polymer Network (IPN) Hydrogel from Natural Rubber and Cassava Starch

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Abstract

Interpenetrating polymer network (IPN) hydrogel based on crosslinked natural rubber (NR) latex and crosslink cassava starch (St) was successfully prepared by a solution blending technique. Crosslinked NR latex was firstly prepared in emulsion state at 70°C by using potassium persulfate as initiator and N, N'-methylene-bis-acrylamide (MBA) as crosslinker. Secondly, the crosslinked NR latex was mixed then with gelatinized cassava starch and maleic acid (MA) as crosslinker for starch at ambient temperature by using mechanical stirrer. Finally, the mixture was casted on a glass mould to form IPN NR/St sheet via crosslinked reaction at 120 ^{o}C in oven for 1.5 h. The water absorption, tensile properties, gel and soluble fraction in water as well as biodegradation of IPN NR/St hydrogels were investigated. It was found that water absorption, soluble fraction, biodegradation and tensile properties decreased with increasing NR contents, while gel fraction in water and elongation at break increased. This was because the rubber molecules prevented the hydrogel from dissolution in water and degraded by microorganism. Furthermore, by immersion of IPN NR/St for long time, water absorption of hydrogel increased with increasing rubber contents due to the effect of elasticity of rubber molecule to easy expansion of INP NR/St hydrogel.

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Keywords: Hydrogel, Natural rubber, Interpenetrating polymer network (IPN), Biodegradation

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1. INTRODUCTION

Nowadays, hydrogel is an important polymeric material that retains large water into their structures because they have hydrophilic groups [1] such as carboxylic and hydroxyl groups etc., appropriately crosslinked in polymer structure. Polyacrylic acid derivatives, polyacrylamide, polyvinyl alcohol and other hydrophilic polymers with little crosslinks are used to produce hydrogels that are the raw materials from petroleum-base chemicals which are wastage materials. Many researchers have interested to improve water absorption of natural rubber (NR) that is a popularly elastic material and a renewable resource and uses to widely applications such as tire, glove, condom etc. NR is a hydrophobic polymer and high elasticity but its structure has unsaturated double bonds which can be degraded from heat, UV, O_2 and ozone. However, the modification of NR can be performed via double bond on main chain of NR such as epoxidized NR (ENR), hydrogened NR and grafted copolymer of vinyl monomer onto NR. From this point, Khongtong et al. [2] prepared water swollen natural rubber by grafting maleic anhydride onto natural rubber chains and Riyajan et al. [3] grafted the modified cassava starch onto natural rubber to improve the hydrophilicity and biodegradation of NR. They reported that this method could change the hydrophobicity to little hydrophilicity of NR. Interpenetrating polymer network (IPN) is one technique to combinations of two or more polymer networks. The entanglements of two crosslinked polymers lead to force 'miscibility' compared to usual blends [4]. The aim of IPN technique is to obtain material with better mechanical properties, increased resistance to degradation and a possibly improved combination of the properties of their components. Hydrogels are polymeric networks that can be synthesized by IPN technique to improve the mechanical properties of that at the swollen states [5]. The preparation of biodegradable hydrogels from NR and cassava starch is a good choice to use binary components because their structures are originally formed from D-glucose unit with hydroxyl group (-OH) which are directed outside of the ring [6]. Several researches have reported the synthesis of biopolymer-based super-absorbent hydrogels from cassava starch and poly(sodium acrylate-co-acrylamide) [7] and cassava starch-g-acrylonitrile hydrogel [8]. Besides, the grafting starch onto natural rubber molecules enable the degradation of NR in soil [3].

The present study intended to develop the IPN hydrogels from natural rubber and cassava starch. The hydrogels were prepared by latex blending technique and used MBA and MA as crosslinkers for NR and St, respectively. The effects of NR contents on the mechanical, water absorption and biodegradation properties of IPN NR/St hydrogel were investigated.

2. Experimental

2.1 Materials

High ammonia concentrated natural rubber latex (HA latex, 60% dry rubber content) was obtained from Thai Rubber Latex corporation Public Company Limited, Thailand. Cassava starch was purchased from Bigtree intertrade Company, Thailand. Potassium hydroxide was obtained from BHD Laboratory Company, England. Emulvin WA as stabilizer for natural rubber latex was purchased from Lanxess Company, Germany. N,N'-methylene-bis-acrylamide (MBA) as crosslink agent for natural rubber, maleic acid as crosslink agent for starch and potassium persulfate as initiator for crosslinking natural rubber latex with MBA were purchased from Sigma-Aldrich company, USA. Toluene was purchased from Honeywell Burdick & Jackson company, USA.

2.2 Preparation of crosslinked natural rubber latex

Crosslinked natural rubber latex was synthesized with MBA, using potassium persulfate (KPS) as initiator. The 150 g high ammonia natural rubber latex (60% DRC) was introduced into a round bottom reactor along with 100 mL of distilled water. KOH (1phr) and Emulvin WA (5 phr) used as buffer and stabilizer, respectively, were then added while stirring. The mixture was warmed up to 70 ^{o}C and 1 phr of KPS was continually added while stirring for 15 min and then added 1 phr of MBA. The reaction was then allowed to proceed for 2 h under continuous stirring and then the reaction was stopped by cooling down to room temperature.

The gelatinized cassava starch (St) was performed by stirring 25% of cassava starch in distilled water at 80 ± 5 ^{o}C until the mixture became transparent and viscous (about 15 minutes). After cooling, the gelatinized St was mixed with maleic acid at 6% w/w of St and crosslinked natural rubber latex (NR) (with various ratios of dry rubber

and St) and stirred at room temperature for 1 h. The mixture was casted on glass mould and then dried at 60 ^{o}C until weight constant. The crosslinking of St molecules in the mixture was done by heating in an oven at 120 ^{o}C for 1.5 h. The interpenetrating polymer network of natural rubber/cassava starch (IPN NR/St) was then obtained. Finally, to increase the osmotic pressure of IPN NR/St, IPN NR/St was immersed in 1wt% KOH solution for 3 h and then dried in an oven at 60 ^{o}C until weight constant.

2.3 Mechanical test

Tensile strength properties were measured according to ASTM D412 using dumbbell shape specimens. The test was carried out on a universal testing machine (Hounsfield Tensometer, model H 10KS) with a crosshead speed of 500 mm/min and an initial gauge length of 25 mm. The reported values were the average of five replicates for each property test.

2.4 Soluble and Gel fraction tests

The soluble fraction is sum of all water-soluble species. The soluble content was measured by extraction IPN NR/St sample in distilled water. A certain amount of the IPN NR/St sample (e.g 0.10 g) was poured into excess amount of water and dispersed with mild magnetic stirring for 3 h (to reach equilibrium swelling). The swollen sample was then filtered and oven dried until weight constant. The sample weight loss easily resulted in the soluble fraction. The gel fraction of IPN NR/St was calculated by using Equation (1)

$$\text{Sol (\%)} + \text{Gel (\%)} = 100 \tag{1}$$

where Sol and Gel are soluble and gel fraction (%), respectively [9].

2.5 Water absorption

The specimen (2 cm x 2 cm x 0.5 mm) was immersed in distilled water (300 mL) at ambient temperature (25-30 ^{o}C). The samples were removed at specified time intervals and gently blotted with tissue paper to remove the excess water on the surface. The weight of each swollen sample was recorded. Then the samples were dried in an oven at 60 ^{o}C to constant weight. The water swelling and mass loss ratios were calculated by the following equation:

$$\textit{Water absorption}\ (\%) = \frac{(w_2 - w_1)}{w_1} \times 100 \tag{2}$$

where w_1 (g) is the weight of the dried sample and w_2 (g) is the weight of the swellen sample.

2.6 FT-IR spectroscopy

For crosslinked NR samples, the prepared samples were washed by soaking in toluene and occasionally stirred for 24 h. The undissolved portion was then filtered and casted on a glass mould. After that, a casted sample was dried in a 50 ^{o}C hot air oven to constant weight. The films of crosslinked NR and IPN NR/St were recorded using FT-IR spectrometer (Perkin Elmer, 1760X, USA). The measurement mode is attenuated total reflectance (ATR).

2.7 Scanning electron microscopy (SEM)

The surface morphologies of all samples were examined by SEM (Hitachi model S-3400 Type II, Japan). All samples were coated with gold ion before use.

2.8 Biodegradation in soil test

The examination of biodegradation of IPN NR/St was applied from Ref. [3]. The specimen (2 cm x 2 cm) was buried under soil at 7 cm from top soil (Ubon Ratchathani, Thailand). The water was poured into the samples buried in soil every week for three months. Each month, the sample was carefully taken out, washed with many distilled water and then dried at 45 ^{o}C until weight constant being weighed.

3. Results and discussion

3.1 Characterization of crosslinked natural rubber

The crosslinked natural rubber (NR) was synthesized by using MBA as crosslinker and KPS as free radical initiator in latex condition. The properties of NR determined from the crosslink density, the gel and soluble fraction in toluene are shown in Table 1. The crosslink density of crosslinked natural rubber was calculated by using the Flory-Rehner Equation [10].

$$p_c = -\frac{1}{2V_s}\frac{\ln(1-V_r^o)+V_r^o+\chi(V_r^o)^2}{V_r^{o1/3}-\frac{V_r^o}{2}} \tag{3}$$

where p_c is the crosslink density (mol/m^3), V_s is the molar volume of toluene (1.069x10^{-4} m^3/mol) at 25 ◦C, V_r^o is the fraction of rubber in the swollen gel and χ is the interaction parameter (0.39 for NR). It was found that the crosslink density, gel and soluble fractions of NR were 0.82 mol/m^3, 20.92 % and 79.08 %, respectively.

Table 1. The properties of crosslinked natural rubber.

	Gel fraction (%)	Soluble fraction (%)	Crosslink density (mol/m^3)
Crosslinked natural rubber	20.92 ± 0.18	79.08 ± 0.18	0.82 ± 0.00

The structure of NR was confirmed by FT-IR spectroscopy. Both NR and crosslinked NR spectra show the absorption peak at 836 cm^{-1} which can be assigned to the vibration of double bond in backbone of rubber molecules. The peaks at 3200-3600 and 1668 cm^{-1} are the stretching of N-H and C=O, respectively, and can be attributed to acrylamide function [11] in MBA. Thus this indicates the successful preparation of crosslinking natural rubber used MBA as crosslinker via free radical reaction in the latex state.

3.2 The effect of NR contents on the gel and soluble fractions of IPN NR/St

Table 2 shows the effect of NR contents on the gel and soluble fractions of IPN NR/St in water. An increase in NR ratio from 10 to 90 results in the decrease of the soluble fraction of IPN NR/St from 24.50% to 2.75% and enhances the gel fraction of IPN NR/St from 75.50% to 97.25%. The reason is that NR is the hydrophobic polymer which could prevents the water soluble component in IPN NR/St such as starch that dissolved in water. Moreover, the crosslink of IPN NR/St is also an important factor affecting to gel and soluble fractions of IPN NR/St. The reason is that high crosslinking decreases the dissolving of polymer in the solvent.

3.3. The effect of NR contents on the tensile properties of IPN NR/St

The influence of NR contents on the tensile properties of IPN NR/St was also investigated. The tensile strength and elongation at break of IPN NR/St containing various contents of NR from 30 to 90 parts are shown in Fig. 1. IPN NR/St samples with lower NR ratios (10-20 parts of NR) were not prepared for tensile test because the

Table 2. Gel and soluble fractions of IPN NR/St with various ratios of NR and St.

Rubber/Starch ratio	Gel fraction (%)	Soluble fraction (%)
90:10	97.25 ± 0.45	2.75 ± 0.45
80:20	95.68 ± 1.02	4.32 ± 1.02
70:30	94.23 ± 1.55	5.77 ± 1.55
60:40	93.98 ± 0.85	6.02 ± 0.85
50:50	93.55 ± 0.58	6.45 ± 0.58
40:60	91.81 ± 0.45	8.19 ± 0.45
30:70	90.58 ± 2.60	9.42 ± 2.60
20:80	88.53 ± 3.52	11.47 ± 3.52
10:90	75.50 ± 5.45	24.50 ± 5.45

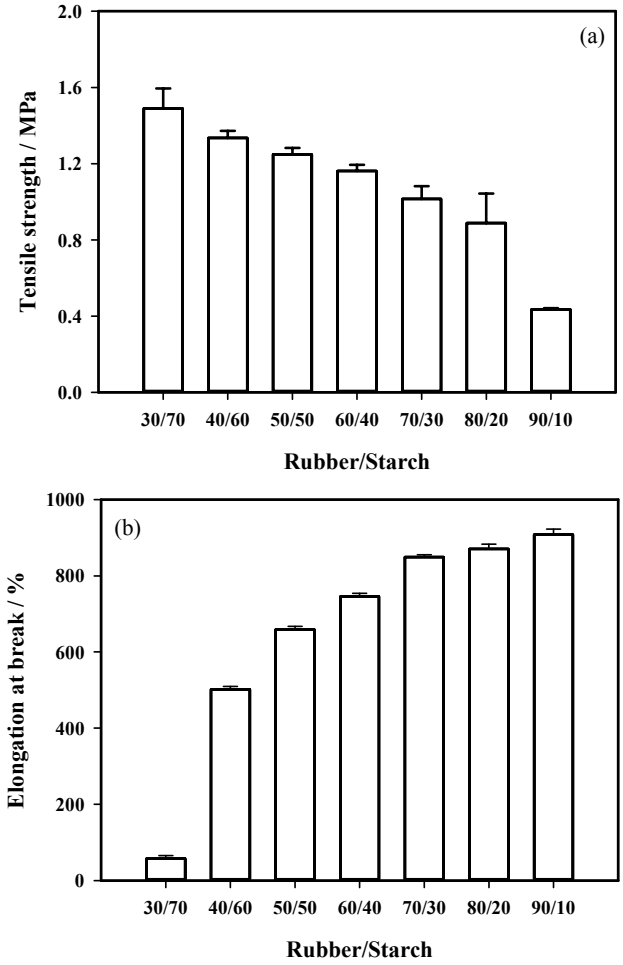


Fig. 1. Tensile properties of IPN NR/St containing various NR contents: (a) Tensile strength and (b) Elongation at break.

samples were cracked during die-cutting. It can be seen from Fig. 1(a) that the tensile strength of IPN NR/St is considerably decreased with increasing of NR contents and yielded a minimum value at the rubber ratio of 90 parts (ca. 0.4 N/mm^2). While, the elongation at break of IPN NR/St is significantly increased with NR contents especially from 30 to 40 parts of NR as shown in Fig. 1(b). The remarkable increase in elongation at break of IPN NR/St from 57% to 908% could be due to elasticity characteristics of NR. Thus, it is observed that the NR contents play significant effects on the both tensile strength and the elongation at break of IPN NR/St samples. Similar behavior was also observed in the thermoplastic starch/natural rubber blends. It was reported that the tensile strength of blends decreased while the elongation at break increased with the addition of rubber [12].

3.4 The effect of NR contents on the water absorption of IPN NR/St

The water absorption of IPN NR/St from 0 to 720 h is presented in Fig. 2. The water absorption of IPN NR/St containing 30 to 90 parts of NR immersed in distillated water for first 24 h is shown in Fig. 2(a). From the start to 12 h, the water absorption of IPN NR/St was decreased with increased NR contents and the maximum value (65.95%) of water absorption was obtained in sample containing 40 parts of NR (60 parts of St). It was anticipated that the hydroxyl group of St with high St contents would promote the superior water absorption of IPN NR/St owning to the abundance hydroxyl groups which are available for interaction with the water molecules [13].

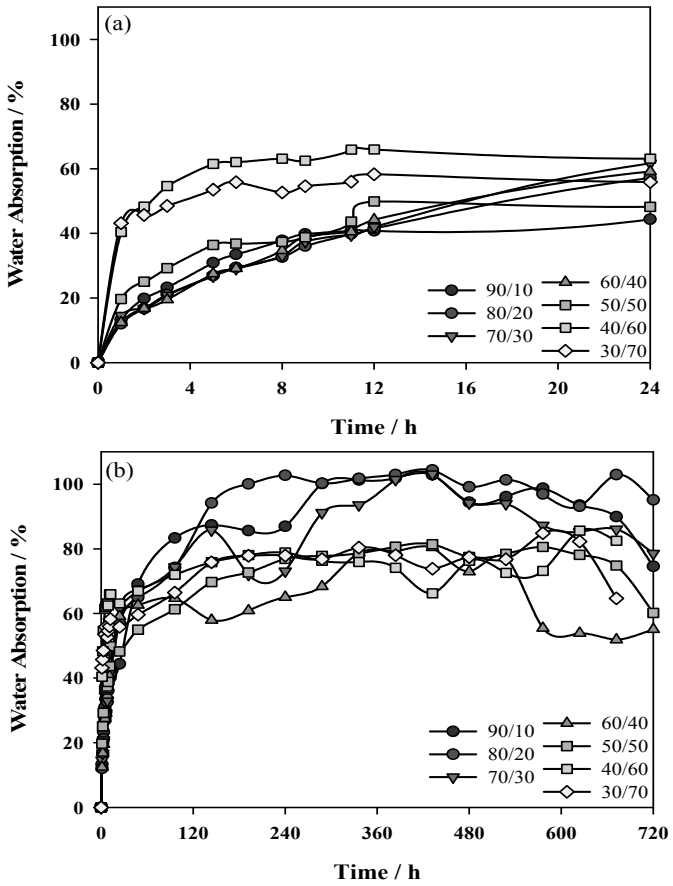


Fig. 2. The effect of NR contents on the water absorption during (a) 24 h and (b) 720 h.

However, after immersion >100 h, the water absorption of IPN NR/St was increased instead with increased the NR content as shown in Fig. 2(b). The maximum value of water absorption of IPN NR/St was enhanced ca. 102.75% at 80 parts of NR at 240 h. This was because after the hydroxyl groups of St absorbed plenty of water molecules into IPN NR/St structure, the molecular chains could easily expanded and could retained large volumes of water. This behavior was supported from the elasticity of polymer. However, at above 80 parts of NR, the water absorption of IPN NR/St decreased slightly because there are lower St molecules in the hydrogel. In addition, Guilherme et. al. [14] also reported that hydrogel presented high water absorption due to the flexibility and hydrophilicity of the polymer network.

3.5 The effect of NR contents on the biodegradation of IPN NR/St

The weight reduction of IPN NR/St with various NR contents degraded in soil was also examined as shown in Fig. 3. It is found that the biodegradation of IPN NR/St linearly decreases with increasing the NR contents. The maximum value of biodegradation of IPN NR/St (30/70 ratio) was obtained about 66% at the 3rd month. The rate of biodegradation of IPN NR/St with high St contents was faster than that of IPN NR/St contained high NR contents because St molecules can be easily degraded by bacteria and fungi in soil [3]. For NR degradation, it was reported that NR slowly degraded in nature by specific microorganisms [15].

Furthermore, to observe the morphology of IPN NR/St samples after buried under soil for 1 month, SEM micrographs were performed and are shown in Fig. 4. It can be seen that there are many holes in rubber matrix. These holes are the granular St dispersed in NR matrix. Therefore, it can be confirmed that NR can be used to reduce the degradation of St.

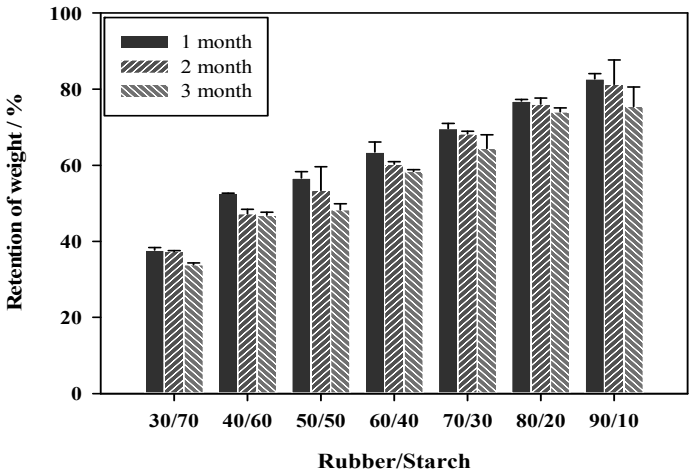
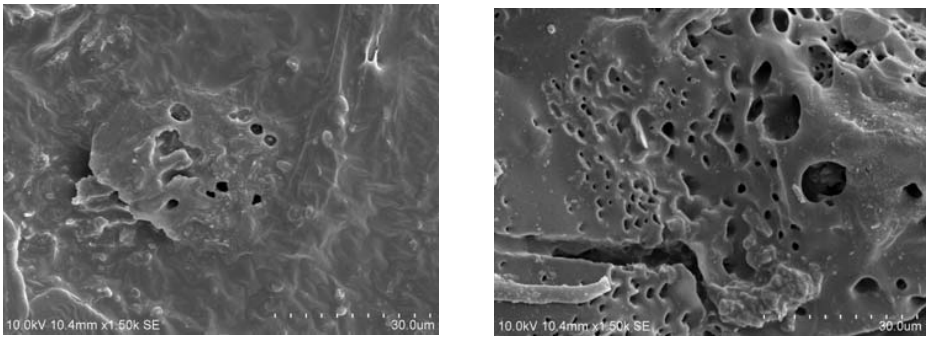


Fig. 3. The effect of NR contents on the biodegradation of IPN NR/St.



(a) (b)

Fig. 4. SEM micrographs of IPN NR/St with rubber/starch ratio of (a) 50/50 and (b) 70/30 after buried under soil for 1 month.

4. CONCLUSION

The IPN NR/St was successfully prepared by mixed crosslinked NR and crosslinked St using MBA and maleic acid as a crosslinker for NR and St, respectively. The tensile strength of the IPN NR/St was found to decrease with the increase of the NR contents and yielded a minimum value at the rubber ratio of 90 parts. Conversely, the elongation at break of IPN NR/St was significantly increased with increasing of the NR contents, especially at lower range of rubber contents (30-50 parts of rubber). At the first 12 h, the water absorption of IPN NR/St was decrease with increased NR contents. It was anticipated by the hydroxyl group of St which would promote the water absorption of IPN NR/St. While after 100 h, the water absorption of IPN NR/St increased stead with increase the NR contents because the hydroxyl group of St after absorption of abundance water molecules into IPN NR/St structure resulted in the easy expansion of molecular chains and can retain large volume of water which supporting from the elasticity of polymer. The biodegradation of IPN NR/St was found to decrease with increasing the NR contents. The rate of biodegradation of IPN NR/St with higher St contents was faster than that of IPN NR/St with higher NR contents. This was due to the easier degradation of St molecules by microorganism in soil and the slower degradation of NR in nature by specific microorganisms. The SEM images of IPN NR/St after buried under soil for 1 month showed many granular holes of St dispersed in rubber matrix. This confirmed that NR can be used to reduce the degradation of St.

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